SCIENCE FOR CERAMIC PRODUCTION

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FLOW PROPERTIES OF SLIP FOR PRODUCING CERAMIC SANITARY WARE

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The effect of a combination of inorganic electrolytes and organic thinners on the flow properties of ceramic slips for casting ceramic sanitary ware is considered. It is shown that adding sodium polyacrylate and a phosphor-bearing component decreases the viscosity, increases the setting rate, and decreases the drying duration.

A topical problem in the production of ceramic sanitary ware is decreasing the moisture and viscosity and increasing the fluidity of casting slip. It is known that ceramic slip should have a preset material and chemical composition of the dispersed phase, possess high fluidity under a minimal moisture level and good filtration properties, and be resistant to stratification.

The most effective method for decreasing the viscosity of a ceramic slip with a constant content of the dispersion phase (water) is the use of liquefying additives (electrolytes), which usually are salts of monovalent metals, as their anions are capable of forming insoluble salts with the cations that make part of the double electric layer on the surface of clay particles. Slip liquefiers are inorganic and organic thinners, whose principle is described in detail in [1 – 4].

At present sodium salts (carbonates, silicates, pyro- and tripolyphosphates, oxalates, etc.) are mostly used in practice. The process of diluting finely dispersed clay systems involves the replacement of bivalent cations in the solvate layer of a clay particle by monovalent cations, a significant growth of the electrokinetic potential, and release of a part of the constitution water. The higher the content of exchange cations in the clay, the larger quantity of electrolyte is required.

We investigated a slip used in the production of sanitary ceramics at the Keramin Company (Republic of Belarus). The main technological operations are as follows: pretreatment of raw materials, preparation of casting and glaze slips, casting a product, its setting, drying, glazing, and firing. Sanitary ware is currently produced at the company by casting in gypsum molds or by injection molding into polymer molds.

A peculiarity of casting suspensions for thick-walled sanitary ceramics is their more pronounced thixotropy than in slips for thin-walled products. The increased thixotropy impedes the casting and especially the discharge of the slip but helps to decrease sedimentation during protracted setting in gypsum molds. Thinning affects not only the flow properties of the suspension but also the formation of the preform. The higher the quantity of water, the slower the dehydration and setting of the preform. However, when thinning is not sufficient, the setting process is accelerated, but the quality of the preform deteriorates. Therefore, the content of water and the dispersion of the solid phase should be optimized taking into account subsequent drying and sintering to ensure the maximally high parameters of the product.

The raw materials used in mixtures for sanitary ceramics include clay from the Veselovskoe deposit of the grade Granitik-Vesko (Ukraine), clay Santon L (Italy), Glukhovetskoe kaolin (Ukraine), and other components.

The water content in a clay suspension depends to a great extent on the mineral composition and dispersion of the argillaceous materials, as well as their cation-exchanging capacity. The clay Granitik-Vesko by its mineral composition belongs to the kaolinite-hydromica group and contains kaolinite, hydromica, and monothermite. Regarding its granulometric composition, the clay is finely dispersed and has the exchange capacity of 15 – 30 mg · equ per 100 g of dry clay; the moisture of the suspension is 52% for viscosity 0.05 Pa · sec. The granulometric composition of this clay is as follows (%, here and elsewhere weight content): fraction > 0.05 mm, 0 – 1.50; 0.05 – 0.01 mm, 0.39 – 2.55; 0.01 – 0.005 mm, 0.77 – 2.12; 0.005 – 0.001 mm, 4.22 – 16.29; and

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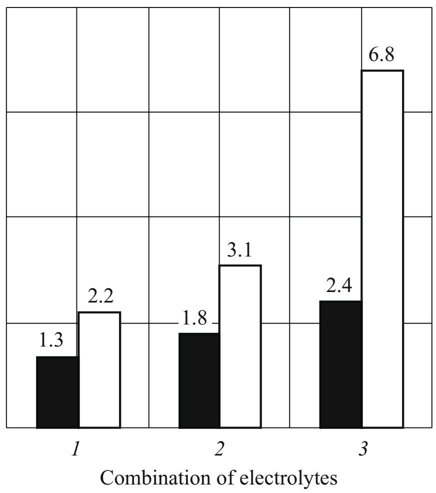

Fig. 1. Comparative characteristics of the industrial slip and surfactant-bearing slips: ■) thickening coefficient; □) relative viscosity (°E); *1*) 0.18% Na_2SiO_3 + 0.10% PP + 0.05% CAR; *2*) 0.18% Na_2SiO_3 + 0.10% SPA + 0.025% Na_2CO_3; *3*) industrial slip.

< 0.001 mm, 79.54 – 92.62. The content of ($SiO_2 + Al_2O_3$) is 74.64%, (CaO + MgO) — 3.35%, calcination loss 9.87%.

The clay Santol L is a medium-plasticity clay (plasticity number 13 – 15) and contains 86.69% ($SiO_2 + Al_2O_3$), 0.36% (CaO + MgO), and 9.01% calcination loss. According to x-ray phase analysis, its phase composition includes α-quartz, kaolinite, illite, and montmorillonite.

The kaolin from the Glukhovetskoe deposit contains 84.71% ($Si_2O + Al_2O_3$), 0.88% (CaO + MgO), and calcination loss 13.38%. The granulometric composition of this kaolin is as follows (%): fraction > 0.05 mm, 0.3 – 0.8; 0.05 – 0.01 mm, 7.0 – 13.5; 0.01 – 0.005 mm, 14.2 – 18.9; 0.005 – 0.001 mm, 16.5 – 23.4; and < 0.001 mm, 41.2 – 64.2. Due to a relatively large quantity of coarse particles (compared to the other types of clay), the kaolin improves the preform setting in the course of slip casting and decreases the air and fire shrinkage of the product. The moisture of kaolin suspension for viscosity 0.05 Pa · sec in the presence of sodium silicates is 38%.

The study of the flow properties of industrially produced slips established that the moisture of the slip for injection molding is 27 – 28%, its relative viscosity 6.8 – 7.0 °E, thickening coefficient 2.4 – 2.54, density 1.83 g/cm^3, preform setting rate 0.315 – 0.321 g/(cm^2 · min), and pH = 8.8 – 9.2. Such viscosity and thickening coefficient are unacceptable for casting in gypsum molds, as they prevent producing high-quality casts.

The study of various combinations and quantities of electrolytes has established that the optimal combination of Na_2SiO_3, the coal-alkali reactant (CAR), and Na_2CO_3 makes it possible to lower the slip viscosity to 3.9 °E and the thickening coefficient to 2.2 and to raise the product setting rate to 0.37 g/(cm^2 · min) and the electrokinetic potential to 42 mV.

In order to improve the flow properties of slips, we have investigated the effect of surfactants, namely sodium polyacrylate (SPA) and a phosphor-bearing plasticizer (PP), which were introduced together with the optimum combination of electrolytes or instead of one of the thinners.

The quality of slips prepared using only inorganic thinners depends on the chemical, mineral, and granulometric composition of the clay materials. The use of only soda ash, soluble sodium glass, and other inorganic agents as electrolytes delays the filtration process, leads to the separation of the cast preform, and narrows the thinning interval. Therefore, thinning agents that are increasingly used lately are organic thinners consisting of a set of salts of mineral and organic acids constituting surfactants and water-soluble polymers. They have a high degree of dissociation, polydispersion, and adsorption capacity, which allows them to be adsorbed on clay particles imparting a negative charge to them. This decelerates the structure formation process in the clay suspension and decreases the thickening coefficient. However, the use of only organic thinners is often not advisable, since the quantity of deflocculants sharply increases, the quality of the preforms deteriorates, and the technological waste increases [5]. Therefore, it is more advisable to use organic thinning agents in combination with inorganic electrolytes.

Figure 1 gives the relative characteristics of the industrial slip and slips containing surfactants. It can be seen that in the case of using only soluble glass, soda ash, and the coal-alkali reactant (the industrial composition) the viscosity of the slip is 6.8 °E with the thickening coefficient 2.4, which makes it difficult to use such slip for casting in gypsum molds. When preforms are produced on casting stands by injection molding, such variant of electrolyte is acceptable.

It is known that the CAR used at the company contains salts of aromatic oxycarbonic acids consisting of carboxyl, carbonyl, and methoxy groups. Owing to them, the reactant can be adsorbed on clay particles, decreases the rate of structure formation, and lowers the thickening coefficient. However, sodium polyacrylate is more efficient. A complete replacement of the CAR by SPA lowers the viscosity to 3.1 °E, the thickening coefficient to 1.8, and raises the preform setting rate to 0.39 g/(cm^2 · min) and the electrokinetic potential to 46 mV.

The maximum improvement of the flow properties of the slip was observed in using two organic thinners, i.e., the CAR and a phosphorus-bearing component: viscosity 2.2 °E, thickening coefficient 1.34, and preform setting rate 0.46 g/cm^2 · min).

It can be seen in Fig. 2 that the use of organic thinners to some extent increases the preform setting rate. The deflocculating effect of sodium polyacrylate is due to its high capacity for adsorption on the surface of mineral particles, which imparts a negative charge and decreases the binding of both interpack water and water on the surface of clay particles [6]. The effect of the phosphate plasticizer is due to the

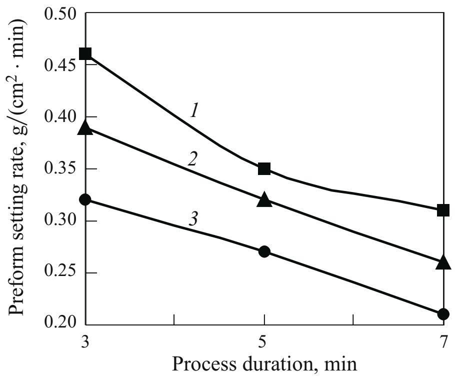

Fig. 2. Preform setting rate versus process duration for the optimal combinations of electrolytes: *1*) 0.18% Na_2SiO_3 + 0.10% PP + 0.05% CAR; *2*) 0.18% Na_2SiO_3 + 0.10% SPA + 0.025% Na_2CO_3; *3*) industrial slip.

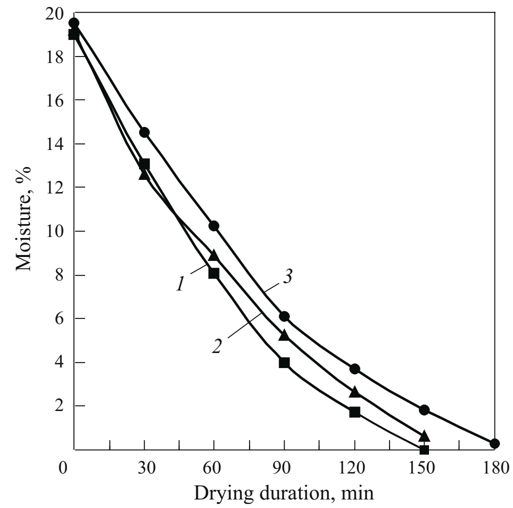

Fig. 3. The effect of surfactants on the duration of product drying. Curve notations the same as in Fig. 2.

presence of a benzene ring and an oxygroup, due to which the adsorption of this component on the surface of clay particles is more complete and prevents the slip from coagulation.

We have also investigated the effect of the additives on drying dynamics. The cast preforms were dried in a drying cabinet at 105 – 110°C to a constant weight and weighed each 30 min. The most intense moisture release was registered in the samples made of the slip with the following combination of electrolytes (%): 0.18% Na_2SiO_3, 0.10 PP, and 0.05 CAR (Fig. 3). The accelerated moisture release is presumably caused by the adhesion between the mineral particles and surfactant molecules, which changes the energy status of water. In the course of drying the surfactant molecules intensely facilitate the cohesion (adhesion) of mineral particles and thus increase the mechanical strength of the cast preform. A constant weight in the preform is reached after 150 min drying; the products made of the industrial slip take the longest to dry.

Thus, the laboratory studies have demonstrated the possibility of improving the flow properties of slips for producing ceramic sanitary ware, increasing the preform setting rate, and decreasing its drying time. The phosphorus-bearing plasticizing agent is not more expensive or scarce than soda ash and water glass, and the implementation of the proposed technology does not require capital investments and can be easily carried out.

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